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## Low adhesion effect of novel duplex NC/WC:C coatings against ductile materials at elevated temperatures

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**Abstract:** A novel anti-adhesive NC/WC:C surface processing is presented enabling green machining of ductile materials at elevated temperatures. The duplex coatings are produced by the active screen plasma nitrocarburising followed by physical vapour WC:C deposition. Microstructure analysis showed that duplex NC/WC:C system is composed by a nanolayered low adhesive WC:C coating and an extra load-bearing NC hardened case, obtaining favourable frictional properties at elevated temperatures. The coefficient of friction of duplex coating NC/WC:C was significantly lower compared to sole WC:C coating or untreated surfaces, and as demonstrated, depending on the testing temperature non-linearly, including an ultra-low adhesion at 350 °C. Furthermore, the quantified adhesion rate is clearly correlated with the nanomechanical properties especially the elastic parameters.

**Keywords:** adhesion, tool coating, plasma nitriding, deposition, wear and tribology, aluminium

### 1. Introduction

Ductile materials such as aluminium alloys tend to adhere with other metals during machining, because the high adhesion energy of interface is enhanced by the energy dissipation from plastic deformation of ductile materials. At elevated temperatures, the adhesion increases with the lower alloy strength and more ductile microstructure and caused particular difficulties to achieve high-quality machining without clogging of tools. In order to reduce adhesion, surface engineering treatments, using hard-facing [1], chemical vapour deposition (CVD) carbides [2] and ceramic coatings [3-5] have been extensively applied to tool surfaces. In general, these treatments can only reduce the wear of tools by increasing hardness of substrate. They have little effect on the chemical affinity and reducing of the materials transfer.

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Carbon based diamond-like carbon (DLC) [6, 7] and nano-C thin film [8] are the most used self-lubricious coatings, attribute to the low affinity of carbonaceous coating to most of the metals including aluminium alloys. However, there are two critical problems associated with these techniques that need to be addressed in order to use them at elevated temperatures: i) the reduction of surface lubricity upon multi-cyclic thermal loading due to degradation of coatings [9, 10]; and ii) the reduction of coating strength at elevated temperatures for a single-layer thin coating [11], especially on a relatively softer deposition substrate where the stress concentration is higher. In this study, a new surface system using plasma nitrocarburised (PNC) substrate combined with a W-stabilised carbonaceous coating was proposed providing thermally stable and super lubricious surface properties. Tungsten adding to the carbonaceous coating showing a phase transformation to oxide forms is lubricious at an interesting temperature range. Here we demonstrate that duplex treatment of active screen PNC substrate and physical vapour deposition (PVD) of WC:C multilayer results in improved low adhesion property and load-bearing capacity compared to sole WC:C coating at elevated temperatures.

## 2. Material and methods

A carefully designed self-lubricant NC/WC:C coating was prepared by low-temperature plasma nitrocarburising followed by cathodic arc physical vapour deposition on substrate of cast iron *NAAMS* G3500. During plasma nitrocarburising, polished and acetone cleaned cast iron was positioned on a cathode work table, and a steel mesh is used as the anode to form plasma. A schematic drawing of the Klöckner (40 kW, Germany) system has been reported in [9, 10]. A gas mixture of 50% H<sub>2</sub>, 48% N<sub>2</sub> and 2% CH<sub>4</sub> was used as N and C source and the process is conducted at a pressure of 4 mbar at 575 °C for 4 hours. The second step of the W-doped carbonaceous mattress coating (WC: C) was deposited by MZR 323 METAPLAST semi-industrial PVD machine (Asociación de la Industria, Spain), which is equipped with two opposing columns of W and C targets each holding three vertically aligned 10 cm pure material cylinders as cathodes. A Cr-based bonding layer was deposited prior to the coating to enhance the bonding strength with the cast iron substrate. The nitrocarburised cast iron was then surface cleaned for 30 min and deposited with WC:C coating for 1-2 hours.

The multi-layer structure of NC/WC:C coating were examined by a field-emission scanning electron microscope (FE-SEM, JEOL 7000). Crystallography was identified via X-ray diffraction (XRD). The

structural morphology of carbon in NC/WC:C was measured on a Renishaw Raman Microscope with a 488 nm excitation and a power of 2 mW. Nano-hardness ( $H$ ) and Young's modulus ( $E$ ) of coatings were measured on polished samples using nanoindentation (Micro Materials Ltd), with the load control mode and a maximum load of 50 mN and increment of 0.5 mN/s. Adhesion resistance, and coefficient of friction ( $CoF$ ) of treated and untreated cast irons was tested by sliding against the aluminium ball using a ball-on-disk linear reciprocating tribometer (TE79, Phoenix tribology, UK). Both aluminium and disc were heated in a chamber and hold for 10 mins before each test. The adhesion rate was quantified and the correlation of adhesion rate and the mechanical data of the coating was implemented in R.

### 3. Results and discussion

The top and transverse microstructures of NC/WC:C coating compared to the sole PNC or WC:C coating after duplex treatments is shown in Fig. 1. It can be seen that PNC surface in Fig. 1a appears rough and 'suttle' due to the strong plasma sputtering on the graphite phase. This sputtering can clean the oxides residue from the surfaces and ensure a better bonding to the subsequent overlayer. Fig. 1d and Fig. 1e showed that the sole WC:C coating was directly deposited on perlite whereas duplex NC/WC:C coating was built on a deep PNC case. Close observation of WC:C overlayer can see a three-tiered lamellae structure with each layer composed of many nanometre sublayers with the thickness of approximately 50 nm. In order of the distance from the surface, the coating is separated to three tiers (groups of layers): C-rich superlubricity tier, W-rich thermal stable tier and a Cr bonding layer. The columnar structures of these three tiers are visible in both secondary electron and back-scattered SEM images.

The XRD patterns of the PNC and composite coating NC/WC:C are shown in Fig. 2. The disappearance of  $\alpha$ -Fe and the appearance of  $\gamma'$ -Fe<sub>4</sub>N and  $\epsilon$ -Fe<sub>2-3</sub>N phases on PNC indicate the development of a hardened case. The XRD of composite NC/WC:C showed a broad peak in the spectra indicating the WC:C overlayer had an amorphous structure. Different with other metal-doped DLC coatings [12, 13], the W-doped WC:C coating remained amorphous and no crystalline of W<sub>1-x</sub>C<sub>x</sub> was formed. The further analysis on Raman in Fig. 5b depicts that NC/WC:C has several underlying bands in the WC:C spectrum. The peak at 1582 cm<sup>-1</sup> is commonly seen for graphite and labelled as G, while the peak at 1480 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> on the shoulders of D and G peak represent highly defected modes of  $sp^2$  and tetrahedral  $sp^3$  bond,

respectively. Compared to conventional DLC coating which has clear D/G peak and smaller D peak, the large defected D/G bands of WC:C are attributed to the reduction in the molecular symmetry of carbon giving more active Raman bands.

The anti-adhesion property of aluminium sliding against treated and untreated cast iron at elevated temperature is displayed in Fig. 3a. At room temperature (RT) the NC/WC:C coating showing a high-to-low transition of  $CoF$  from 0.5 to 0.15 in the first 100 cycles after which it becomes stable and remains 0.15. An increase of temperature from RT to 200 °C raise  $CoF$  from 0.15 to 0.65 and the highly fluctuated  $CoF$  evidenced the continuous adhesion and breaking of the ductile aluminium film on the interface. This rising of  $CoF$  with temperature is perhaps related to the deficiency of the internal passivity of C- bond at dry and hot conditions which has been discussed by many studies [14]. Interestingly, in this study,  $CoF$  of NC/WC:C was not a linear function of temperature, while the  $CoF$  at 350 °C was the lowest and corresponded to 0.15. To this end, it is presumed that the expected phase transformation from a-W:C to  $WO_3$  and  $W_xC_{1-x}$  occurred during heating helps to reduce the friction and adhesion of aluminium [15].

Apart from the chamber temperature, the adhesion of aluminium is also affected by the counterpart materials as shown in Fig. 3b. Untreated G3500 and PNC have a similar level of  $CoF$  corresponding to around 0.7. In comparison, the  $CoF$  of WC:C and NC/WC:C coated surface are significantly smaller, and the lowest  $CoF$  was generated at 350 °C on NC/WC:C without a sign of degradation for 500 cycles. The surface morphologies of contact area in Fig. 3c-d also show that both PNC and untreated G3500 were covered with a layer of aluminium residue, whereas WC:C and NC/WC:C showed the clean and adhesion-free wear tracks on both surfaces in Fig. 3 e-f, which confirmed their low affinity to the aluminium adhesion. Adhesion rate  $K_a$  expressed as the amount of material loss on the contact area  $mm^3/Nm$  was calculated and the corresponding mechanical properties are listed in Table 1. It was found that  $E$  and  $CoF$  are the most effective parameters to the adhesion rate, after analysing notable parameters of elasticity such as  $H/E$ ,  $H/E_r^2$  and  $(H/E)^2$  [16, 17] in the linear regression model. In the well-known wear model modified by Torrance [18], the material with higher elastic strain prior to plastic deformation (i.e.  $H/E$  ratio) is more resistant to deformation from abrasion of non-adhesive materials. This study found that material with low  $E$  will transform the  $k_a$  from negative to positive and alter wear

mechanism from adhesive to abrasive, subsequently, reduce the friction of the ductile material. This study demonstrates that the adhesion resistance of surface treated materials is affected by the microstructure of material at the interface and also by the elastic parameters of the surface.

#### 4. Conclusion

The NC/WC:C hybrid composite coating was designed and synthesised composing of an amorphous a-C:W functional layer, an a-C:W/Ni intermediate layer, a bonding layer and a deeply modified nitrocarburised underlayer. This multi-layered NC/WC:C has improved friction and adhesion resistance compared to sole WC:C coating. The resistance of the duplex coating to adhesion of aluminium alloy is affected by the temperature of counterparts; from room temperature to 350 °C, friction firstly increased and then began to decrease again at 350 °C. Quantified analysis of the adhesion resistance of the coated cast iron was strongly correlated with the mechanical properties especially Young's modulus of the coatings.

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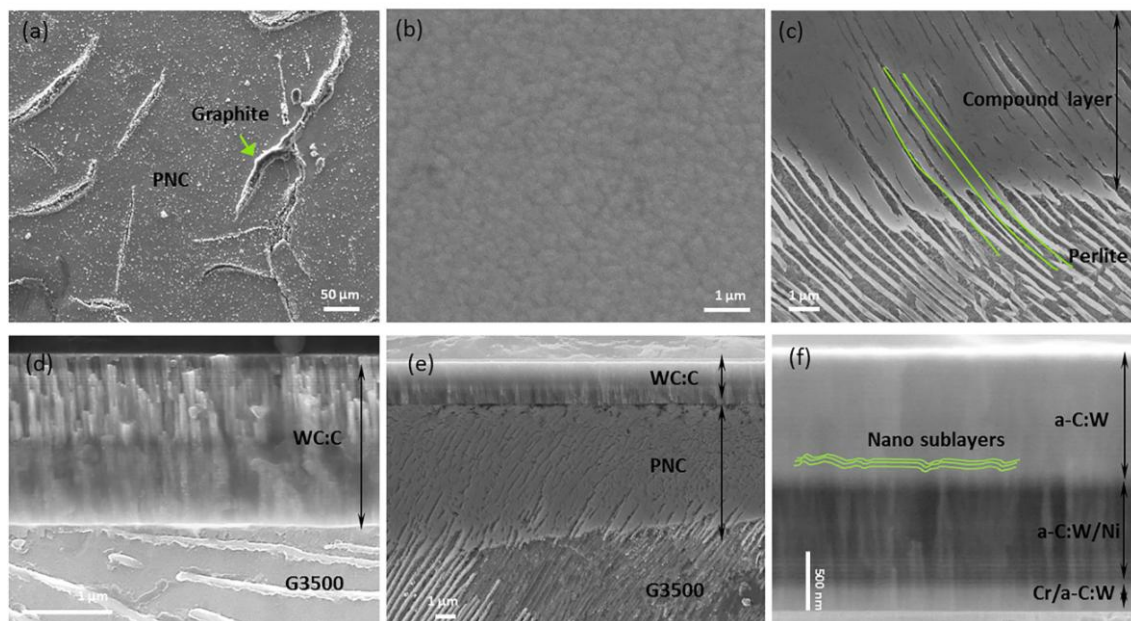
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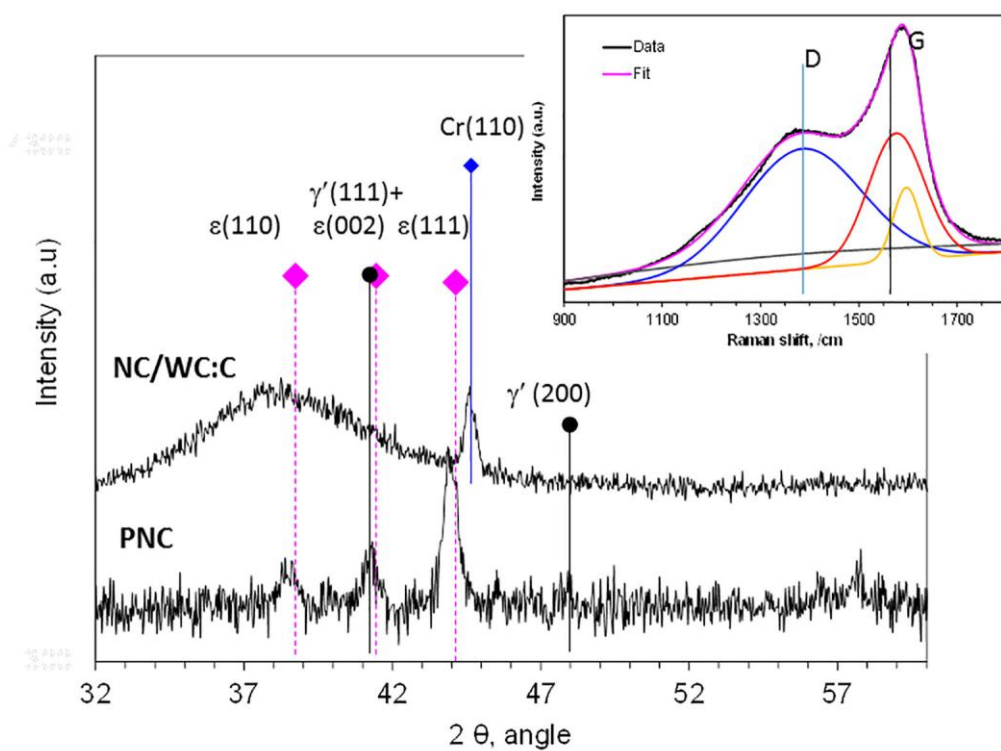


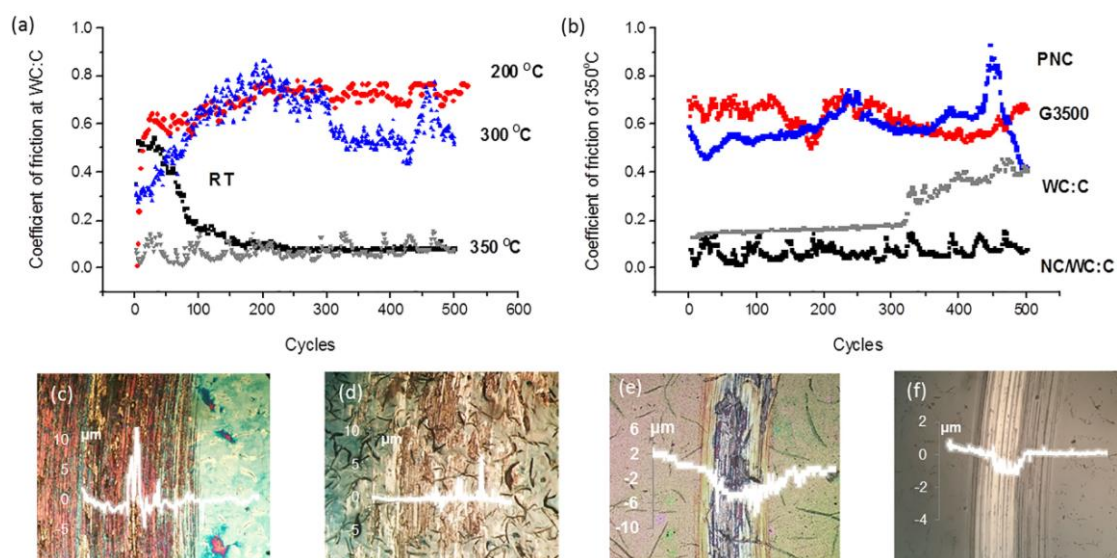
**Fig. 1.** SEM topography of as-deposited (a) PNC and (b) NC/WC:C; Cross-sectional SEM morphology of (c) PNC, (d) WC:C, (e); (f) Back-scattered FESEM image of WC:C.

**Fig. 2.** XRD of coated surface showing ceramic conversion of cast iron on the surface of PNC, and amorphous surface microstructure of NC/WC:C; (insert) Raman spectra of G and D band with curve fitting results overlaid in pink

**Fig. 3.** (a) effect of the temperature of pin-on-disc chamber to the CoF and (b) effect of tool coatings; 3D profilometry and optical image of wear track on (c) G3500, (d) PNC, (e) WC:C and (d) NC/WC:C







**Table 1** Wear rates of the sliding counterparts as compare to the corresponding  $E$  and  $CoF$ 

	$k_a$ (v.s. Al alloy)	E, GPa	H, GPa	$CoF$
G3500	2.99E-06	172	3.66	0.67
PNC	5.65E-06	198	11.07	0.67
WC:C	6.01E-07	102	6.25	0.25
NC/WC:C	9.00E-08	105	6.10	0.15